

2D SAXS/WAXD ANALYSIS OF PAN CARBON FIBER MICROSTRUCTURE IN ORGANIC/INORGANIC TRANSFORMATION*

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Abstract Structure of PAN fibers during pre-oxidation and carbonization was studied using two dimensional small angle X-ray scattering/wide angle X-ray diffraction (2D SAXS/WAXD). The SAXS results show that during pre-oxidation between 180 °C and 275 °C, the volume content of microvoids increases with the temperature increasing, which may be one of reasons for the decrease of tensile strength of pre-oxidized fibers. 253 °C was the critical transition temperature, the length, diameter, aspect ratio and orientation distribution of microvoids increased with temperature before this temperature and decreased after this temperature. After the high temperature carbonization, lots of spindly microvoids formed. WAXD patterns demonstrate that the crystallite size of PAN fibers first increased before 230 °C and then decreased with the increase of temperature during the pre-oxidation. The diffraction peak of PAN fibers at $2\theta \approx 17^\circ$ almost disappeared at the end of pre-oxidation while the diffraction peak of aromatic structure at $2\theta \approx 25^\circ$ appeared at 253 °C. During carbonization, the peak intensity at $2\theta \approx 25^\circ$ increased apparently due to the formation of graphite structure. The results obtained give a deep understanding of the microstructure development in the PAN fibers during pre-oxidation and carbonization, which is important for the preparation of high performance carbon fibers.

Keywords: Polyacrylonitrile; Pre-oxidation; Carbonization; SAXS/WAXD; Microstructure.

INTRODUCTION

Carbon fibers have many merits such as low density, high strength and high elastic modulus and have been widely used as reinforcement materials in various composites. Compared with rayon- and pitch-based carbon fibers, PAN-based carbon fibers have a dominant position in the market due to their lower cost and the mature technology^[1]. The PAN-based carbon fibers are usually prepared *via* pre-oxidation and carbonization of the precursor fibers. During the pre-oxidation process, a series of chemical reactions such as cyclization, dehydrogenation and oxidation occur accompanying with the change of the microstructure, element content and aggregative state in the fibers^[2, 3]. In the carbonization stage, the aromatic ladder structure will undergo further

* The work was financially supported by Innovation Method Fund of China (2011IM030400), NSFC (No. 10835008), the Knowledge Innovation Project of CAS (No. KJXC2-YW-N39), 973 Program (No. 2011CB605604), the Opening Foundation of Shenzhen Key Laboratory of Functional Polymers (FP20120012), Natural Science Foundation of Shenzhen University (Grant no. 201204) and the Shenzhen basic research project (JCYJ20120614085820810).

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Invited paper dedicated to Professor Fosong Wang on the occasion of his 80th birthday

Received December 26, 2012; Revised January 25, 2013; Accepted January 31, 2013

doi: 10.1007/s10118-013-1272-1

cross-linking, cyclization and condensation, leading to the formation of turbostratic graphite structure^[4]. Finally, the carbon fibers with more than 90 wt% carbon are obtained with non-carbon elements splitting off.

Many investigations have been devoted to the structural evolution of PAN fibers during pre-oxidation and carbonization by scanning electron microscopy, transmission electron microscopy, optical microscopy, Fourier transform infrared spectroscopy, differential scanning calorimetry and so on^[5–9]. However, small angle X-ray scattering as a useful tool due to its penetrability and statistics has been rarely used to characterize the microstructural evolution of pre-oxidation and carbonization. The pre-oxidation has been characterized by Thunemann and Ruland with SAXS to evaluate the formation of lamellar structure and microvoids in PAN fibers^[10, 11]. It has been known that microvoids in carbon fibers play an important role in the fiber mechanical properties, especially the tensile strength^[12, 13]. These microvoids are mainly due to the imperfect packing of ribbons of carbon layers, and also may inherit from precursor fibers or form in the process of pre-oxidation and carbonization^[14]. Therefore, to characterize the evolution of microvoids during the pre-oxidation and carbonization of the precursor fibers is significant for the preparation of high performance carbon fibers.

The major feature of PAN carbon fiber manufacture is organic/inorganic transformation. During this process, the PAN polymer fiber transforms to inorganic fiber containing more than 90% carbon. In the present paper, 2D SAXS/WAXD was carried out to investigate the transformation of microvoids and crystallite structure during the pre-oxidation and carbonization processes of PAN fibers. The information obtained may provide new clues to understand the structure evolution in the formation of carbon fibers. Although the samples used in our work were *ex-situ* fiber bundles after each processing step, the results obtained can veritably reflect the structure change during the industrial production of carbon fibers to some extent.

EXPERIMENTAL

Materials

PAN fibers with each single tow containing 3000 filaments were provided by Shanxi Hengtian New Textile Fiber Tech Co., Ltd. China, and a single filament had quality indices of 1.00 dtex in titre, 5.6 cN/dtex in tensile strength and 11% in elongation. The stabilization proceeded in an oxidizing furnace with five temperature zones, and the applied stretch ratio at each temperature zone was shown in Table 1. It should be noted that during high temperature carbonization the stretching tension was less than the constriction force resulting from thermal shrinkage, and the minus stretching ratio meant the shrinkage of the fibers happened at this stage.

Table 1. The processing parameters of pre-oxidation and carbonization

	Pre-oxidation					Carbonization	
	Initial stage		Later stage			Low temperature	High temperature
Temperature (°C)	180	212	230	253	275	350/480/580/780	1300
Stretching ratio (%)	2	2	1	0	0	3	–3

Measurements

Small angle X-ray scattering measurements were carried out with a Rigaku S/Max 3000 SAXS/WAXD system with rotating anode X-ray generator equipped with two laterally graded multilayer optics in a side-by-side arrangement, emitting a highly focused parallel beam of monochromatic CuK α radiation ($\lambda = 0.15418$ nm). The beam, operated at 40 kV and 30 mA, was collimated using three pinholes and the beam diameter at the sample position was approximately 70 μ m. Two dimensional SAXS patterns were collected by a gas-filled multiwire detector at 1500 mm from sample position, and the scattering vector q was calibrated using silver behenate powder, with (001) peak position at 5.838 nm. The information of wide angle X-ray diffraction was collected by Image Plate. The fibers were measured as aligned multifilament bundles, which were fixed in the horizontal direction.

RESULTS AND DISCUSSION

SAXS/WAXD Analysis

The SAXS patterns of the fibers at various stages of pre-oxidation and carbonization are shown in Fig. 1. The fibers are fixed in the horizontal direction, and the scattering lobes with a scattering maximum are extended in the vertical direction, which reflect the preferential orientation of the long axes of microvoids in the fibers with respect to the machine direction. The parameters of microvoids, such as size, shape and content, in the fibers can be obtained from SAXS patterns by the method developed by Ruland *et al.*^[10]. Ruland's streak method has been successfully used to analyze microvoids in carbon fibers^[12, 15, 16–18] and pre-oxidized PAN fibers in the temperature range from 190 °C to 470 °C^[10, 11]. Gao *et al.*^[19] has evaluated the effect of tension on the microvoids' structure during the thermal stabilized process. Herein, we employed the method to analyze the fibers at various stages during pre-oxidation and carbonization. All scattering patterns were fitted at same region to increase the reliability of the relative comparison. For each section, the integral breadth was determined by all data points within the section using the azimuthal scan. The representative plot of the linear fitting is depicted in Fig. 2(a), which indicates that the data fit well with Gaussian distribution function in the chosen region for Ruland's model.

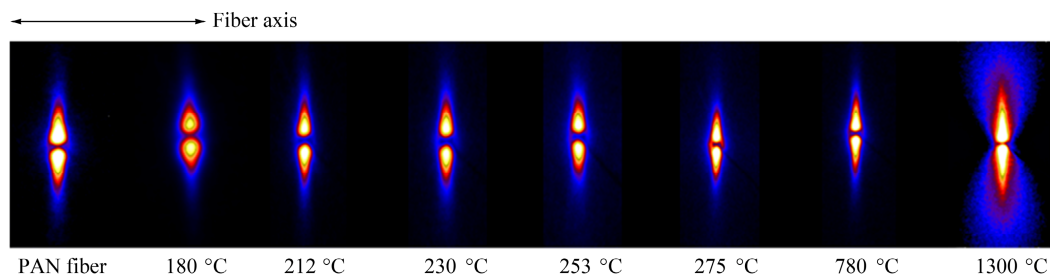


Fig. 1 2D SAXS patterns of the fibers at various stages of pre-oxidation and carbonization

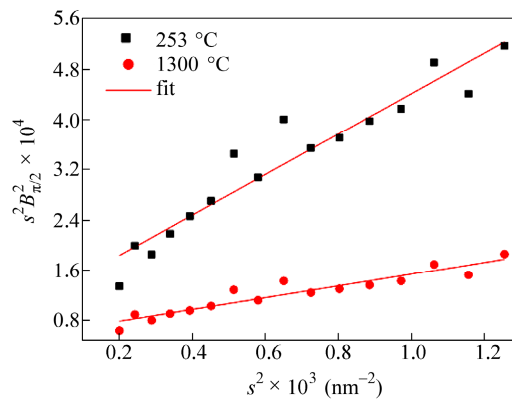


Fig. 2 Plots of $s^2 B_{\pi/2}^2 (s)$ versus s^2 of samples treated at 253 and 1300 °C fitted with Gaussian distribution function according to Eq. (2)

According to the reported calculation method^[10], the length of the microvoids L , the width B_{eq} of the equatorial orientation distribution of the microvoids and the average chord length l_p in the cross section of the microvoids can be obtained from Eqs. (1–4)

$$I(s) = F(\Delta\rho^{*2}) \quad (1)$$

in which $I(s)$ is scattering intensity in reciprocal and s equals to $2\sin\theta/\lambda$, F stands for the three dimensional Fourier transform, $\Delta\rho$ is the electronic density difference between the local electron density and the average electron density, and $\Delta\rho^{*2}$ is self-convolution or autocorrelation of electronic density difference.

$$s^2 B_{\pi/2}^2(s) = 1/L^2 + s^2 B_{eq}^2 \quad (2)$$

$B_{\pi/2}(s)$ is the integration breadth along azimuthal scan.

$$I(s, \pi/2) \propto n \rho_m^2 \frac{L^2}{\sqrt{1 + (s L B_{eq})^2}} |\Phi_D|^2(s) \quad (3)$$

$$|\Phi_D|^2(s) \propto \frac{l_p^2}{[1 + (2\pi l_p s)^2]^{3/2}} \quad (4)$$

The values of L and B_{eq} can be obtained from the intercept and slope of the $s^2 - s^2 B_{\pi/2}^2(s)$ plot (as shown in Fig. 2, samples treated at 253 and 1300 °C are selected as examples). After this, the parameter l_p and the relative number n of microvoids were obtained *via* Eqs. (3) and (4) by fitting the theoretical to experimental $s-I(s, \pi/2)$ curves. The total volume of microvoids V can be evaluated approximately $V \propto n L l_p^2$ (the relative microvoids volume percent V_{rel} is the ratio of the microvoids volume content in the samples to the pristine fibers).

During the preoxidation and carbonization treatment, PAN fibers underwent a series of physical and chemical changes. In this process, the parameters of microvoids in the fibers also changed as shown in Fig. 3.

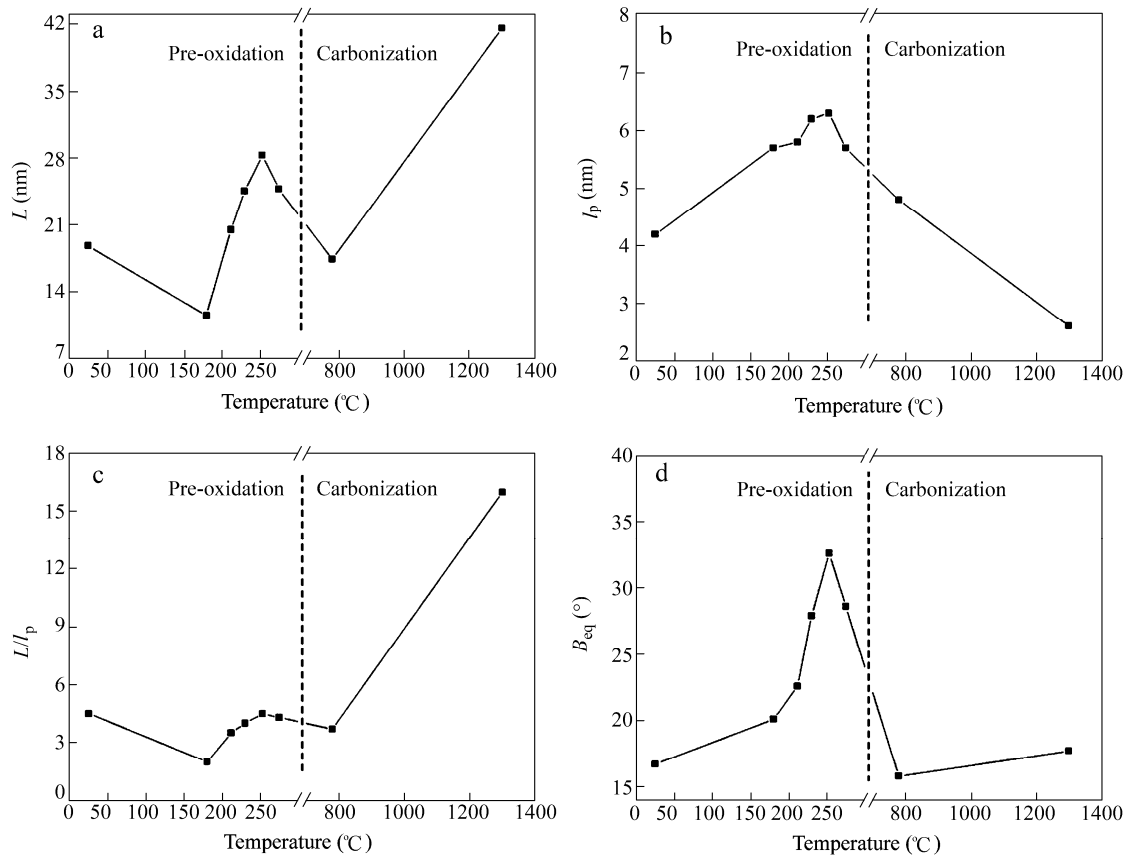


Fig. 3 The length L , average chord length l_p in the cross section, L/l_p and the width B_{eq} of the equatorial orientation distribution of the microvoids in the fibers at various stages during pre-oxidation and carbonization (assuming that the PAN precursor fiber is at 25 °C)

The length L of microvoids of precursor PAN fiber is 18.8 nm, after treatment at 180 °C, it decreases to 11.5 nm, which results from thermal shrinkage. After this temperature, L increases monotonously to an extreme value, and then decreases with the temperature increase. The average chord length l_p in the cross section and the preferred orientation of microvoids as determined by B_{eq} also reach the maximum at 253 °C during pre-oxidation process. As mentioned above, 230 °C is a turning point of pre-oxidation where fiber structure begins to transform obviously, and 253 °C is a key point for the evolution of microvoids in fibers during pre-oxidation. The later XRD results show that at 253 °C PAN crystallite structure and ordered arrangement of aromatic ladder structure coexist, which may induce the large average microvoids size in the fibers. In addition, the average microvoids size decreases at 275 °C which may be due to the disappearance of PAN crystallites and the formation of more uniform structure. After low temperature carbonization, the length and aspect ratio of microvoids decrease because of the rearrangement and compactness of structure along the fiber axis. After high temperature carbonization, L increases and l_p decreases drastically, which mean that the obtained carbon fibers have spindly microvoids with high aspect ratio L/l_p of 16.0. This is in agreement with the results observed elsewhere^[20]. Although minus stretching ratio is applied at this stage, thermal shrinkage in cross section is larger than that along the fiber axis at 1300 °C, generating spindly microvoids.

It can be noted that the equatorial orientation distribution B_{eq} of microvoids changed by almost 20° (from 16.7° at RT to more than 32.6° at 253 °C and back to about 17.7° at high temperature, as shown in Fig. 3d). However, for the azimuthal spread of the SAXS streak, it seems that the largest value of B_{eq} is at 1300 °C, not at 253 °C. According to the Ruland's streak method, $B_{\pi/2}(s)$ is the integration breadth along azimuthal scan defined as

$$B_{\pi/2}(s) = \frac{1}{I(s, \pi/2)} \int I(s, \phi) d\phi \quad (5)$$

Here the numerator is the integration of intensity at different scattering vectors s , and denominator is the scattering intensity sliced along the streak center of the pattern. Therefore, the integration breadth at different s correlates with $I(s, \phi)$ and $I(s, \pi/2)$. Although the 2D SAXS scattering pattern at 1300 °C spreads wider than the one at 253 °C, the larger scattering intensity sliced along the streak center of the pattern counteracts the effect of the spread. Given the fact that B_{eq} just describes the orientation angle of microvoids statistically, the orientation angle of microvoids is able to change by about 20°, as demonstrated in Ref. [10]. In addition, the width B_{eq} of orientation distribution may be influenced by the orientation distribution of the fibers in the bundle, which would tamper the results. To eliminate the misalignment of fiber in bundles, independent fiber bundles after each processing step were aligned to parallel to each other as well as possible before the measurement, and the measurement for each sample was repeated for three times.

During the pre-oxidation process, the tensile strength of preoxidized fibers usually decreases with the increase of temperature^[3]. The general explanation contains two aspects: on one hand, the cohesive energy between the relative chains drops a lot because $C \equiv N$ with high polarity gradually converts into $C = N$ with the formation of ladder structure; on the other hand, the orientation of molecular chain along the direction parallel to the fiber axis decreases with the temperature increasing, leading to the disordered molecular arrangement^[21]. From the results of SAXS, we find that the volume content V_{rel} of the microvoids, as shown in Fig. 4, increases with the temperature increasing during pre-oxidation which may be another reason for the decrease of mechanical properties of the oxidized-fibers. Interestingly, the carbon fibers obtained after high temperature carbonization have the highest volume content among all the samples. Because of the splitting off of non carbon elements, new microvoids may be produced^[5]. However, the carbonization process results in cross-linking between adjacent chains which may account for the increase in tensile strength of carbon fibers^[22]. Therefore, the high tensile strength of carbon fibers can be explained by the large L/l_p of the microvoids and the formation of turbostratic graphite structure at 1300 °C.

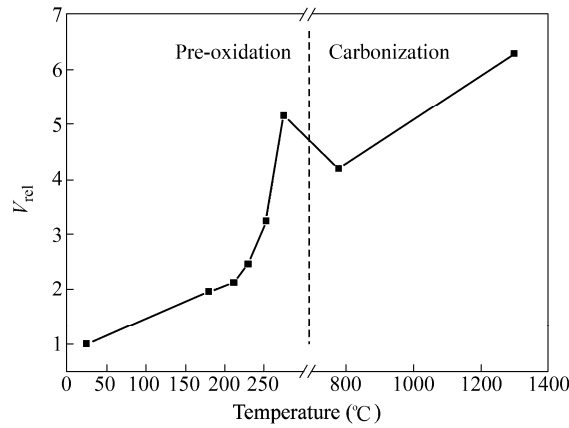


Fig. 4 The relative total volume V_{rel} of microvoids in the fibers at various stages during pre-oxidation and carbonization

Additionally, the WAXD patterns of the fibers at various stages of pre-oxidation and carbonization are shown in Fig. 5, which reveal that the crystallites of PAN and turbostratic structure of carbon fibers are oriented along the fiber axes. The crystallite size (L_c) was calculated from the Scherrer formula:

$$L_c = \frac{K\lambda}{B \cos \theta} \quad (6)$$

in which λ is the wavelength of CuK α X-ray, B is the full width at half the maximum intensity (FWHM) of the (100) peak at around $2\theta \approx 17^\circ$ for PAN precursor fibers and pre-oxidized fibers, and the (002) peak at $2\theta \approx 25^\circ$ for carbon fibers, and K is a constant, assigned as 0.89. The lattice spacing (d) was calculated from the Bragg equation:

$$2d \sin \theta = n\lambda \quad (7)$$

in which $n = 1$, $\lambda = 0.15418$ nm and θ is the half of the diffraction angle. The crystal lamellar orientation factor F^c is defined as Ref. [13], which reflects the orientation distribution of the chain axis based on reciprocal lattice vector of the lattice plane (100) for crystallites in PAN fibers and (002) for graphite in carbon fibers, and can be obtained from Eqs. (8–10). The results obtained from WAXD patterns are summarized in Table 2.

$$F^c = 2 - 3 \langle \cos^2 \theta_j \rangle \quad (8)$$

$$\langle \cos^2 \theta_j \rangle = \int_0^{\pi/2} q_j (\cos \theta_j) \cos^2 \theta_j \sin \theta_j d\theta_j \quad (9)$$

$$q_j = \frac{I(\theta_j)}{\int_0^{\pi/2} I(\theta_j) \sin \theta_j d\theta_j} \quad (10)$$

in which θ_j is the angle between the reciprocal lattice vector of the lattice plane and the machine direction; $I(\theta_j)$ is the diffraction intensity distribution of the reciprocal lattice vector of the lattice plane; q_j is the orientation distribution function of the reciprocal lattice vector of the lattice plane.

As shown in Fig. 5 and Fig. 6, two peaks appear at $2\theta \approx 17^\circ$ and 29° in the XRD patterns of PAN fibers and the pre-oxidized fibers at the initial stage, corresponding to the (100) peak and (110) peak^[23]. The intensity of these two peaks is slightly strengthened below 230 °C. Correspondingly, the crystallite size of pre-oxidized fibers treated at 180 and 212 °C increases, which may be due to stretching and heatin^[5]. The pre-oxidation

reactions first proceed in the amorphous domain, where the polymer chains stack loosely and disorderly and dominant chemical reaction has not happened at such low temperatures. When the temperature is higher than 230 °C, the intensity of these two peaks begins to weaken rapidly, suggesting that the pre-oxidation reactions such as oxidation and cyclization have started to proceed in the crystalline domain. The linear molecular chains begin to change into aromatic ladder structure. A wide and flat diffraction peak centered at 25° appears at 253 °C, indicating the existence of ordered arrangement of aromatic ladder structure, while the intensity of diffraction peak at $2\theta \approx 17^\circ$ of PAN further decreases. At the end of pre-oxidation, the PAN crystalline structure almost disappears and the obtained pre-oxidized fibers show an amorphous X-ray pattern. During carbonization, the structure of pre-oxidized fibers changes from essentially amorphous to partly crystalline after high temperature treatment; the peak at $2\theta \approx 25^\circ$ gradually strengthens with the increase of temperature, demonstrating that the graphite structure in the carbon fibers gets more and more perfect^[24].

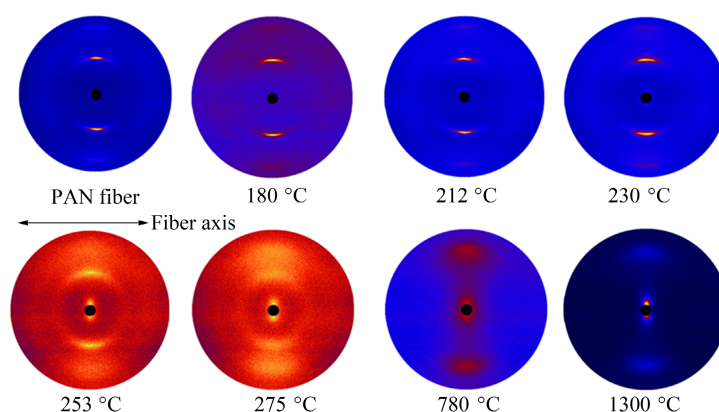


Fig. 5 The WAXD patterns of the fibers at different temperatures during pre-oxidation and carbonization

Table 2. The results calculated from the WAXD measurements of samples at different stages

	2θ (°)	d (nm)	FWHM	L_c (nm)	Orientation factor F^c
PAN fiber	17.0	0.5	1.2	6.8	0.95
180 °C	16.9	0.5	1.1	7.2	0.93
212 °C	16.9	0.5	0.9	9.0	0.95
230 °C	16.9	0.5	1.3	6.4	0.92
253 °C	16.8	0.5	2.0	4.0	0.81
275 °C	16.7	0.5	—	—	0.67
	25.3	0.4			
780 °C	25.4	0.4	8.8	0.9	0.77
1300 °C	25.4	0.4	6.4	1.3	0.77

The crystal lamellar orientation factor F^c characterizes the orientation distribution of the chain axis with variation between $-1/2$ and 1. For random orientation, the factor is 0, while for complete orientation parallel and perpendicular to the drawing direction, the factor is 1 and $-1/2$, respectively^[13]. The chain axes of fibers at various stages of pre-oxidation and carbonization orient predominantly parallel to the drawing direction as shown in Fig. 5 and Table 2. For PAN fibers, the sharp peak of the (100) plane is observed, and the WAXD pattern indicates the preferential orientation of the chain axis with respect to the machine direction. Therefore, the value of F^c is high. At the initial stage of pre-oxidation, the pre-oxidized reactions occurred mainly in the non-crystalline region, F^c relating to the crystalline region did not change apparently. With the increase of temperature, the PAN crystallites were destroyed gradually and the peak of the (100) lattice plane became

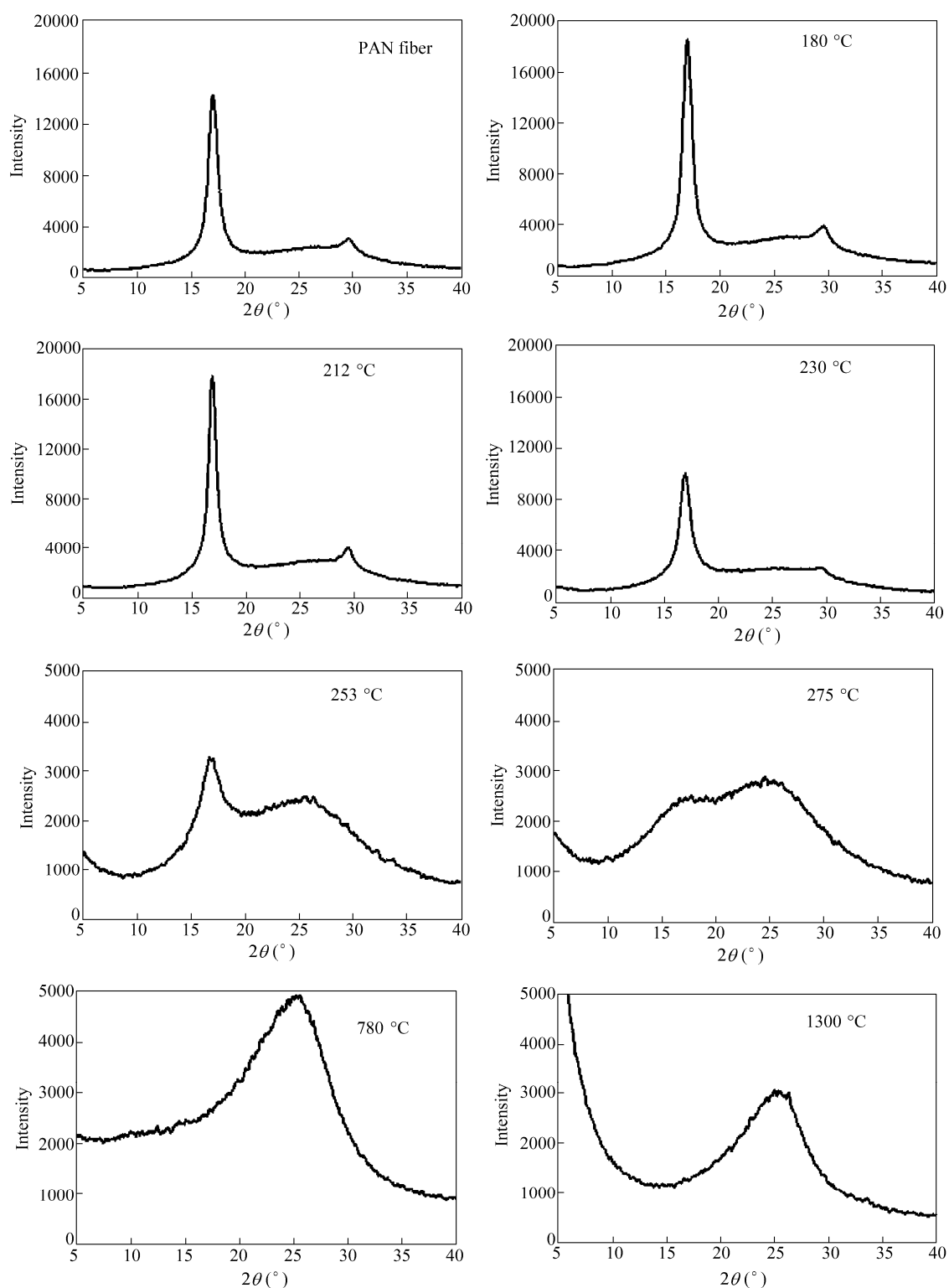


Fig. 6 X-ray diffraction intensity distribution for the fibers at various stages of pre-oxidation and carbonization calculated in the vertical direction from Fig. 5

smaller and broader, leading to the decrease of orientation of the chain axis and decrease of F^c . At the end of pre-oxidation, F^c reached the minimum since crystalline structure of PAN almost disappeared. In the carbonization process, the new peak of the (002) plane concerning turbostratic graphite structure appeared, the orientation of chains enhanced and the value of F^c increased. The variation of crystal lamellar orientation can be observed clearly in Fig. 5. In addition, the change of F^c is also consistent with that of the microvoids during pre-oxidation and carbonization. With the proceeding of pre-oxidation reactions and the decrease of chain orientation, more microvoids formed and the width of the equatorial orientation distribution of the microvoids for the fibers first increased and reached the maximum of B_{eq} , and then decreased when the chain orientation increased at the carbonization stage. In other words, the microvoids orientation distribution parameter B_{eq} had a corresponding but converse change tendency with crystal lamellar orientation factor F^c . Although the values of F^c for PAN precursor fibers, pre-oxidized fibers and carbon fibers in this work are much different from that in Ref. [13], they have the same change tendency, namely the pre-oxidized fibers have the lowest chain orientation and F^c .

CONCLUSIONS

Microvoids and crystallite structure of PAN fibers during pre-oxidation and carbonization have been investigated by 2D SAXS/WAXD for the first time. It shows that the volume content of microvoids increases monotonously with the pre-oxidation temperature. The length, diameter, orientation distribution width and aspect ratio of microvoids increase with the temperature until 253 °C and then decrease. After low temperature carbonization, the length, aspect ratio and relative volume percent of microvoids decrease due to the rearrangement and compactness of molecular chains. After high temperature carbonization, however, non-carbon elements split off, leading the volume content of microvoids to increase; and the thermal shrinkage along the direction perpendicular to the fiber axis results in the formation of spindly microvoids. In addition, the crystallite structure of the fibers also changes. In pre-oxidation stage, the mean crystallite size of fibers first increases below 230 °C, and then decreases with the temperature increase. The broad peak appearing at $2\theta \approx 25^\circ$ indicates the formation of ordered arrangement of aromatic ladder structure at 253 °C. The coexistence of crystalline structure of PAN and aromatic ladder structure may lead to appearance of the maximum of microvoids parameters. At the end of pre-oxidation, the crystallite structure of PAN fibers is almost damaged. Additionally, the results of 2D SAXS/WAXD demonstrate that 230 and 253 °C are critical transition temperatures: 230 °C is a turning point of pre-oxidation where fiber structure begins to transform obviously, and 253 °C is a key point where series of physical and chemical changes occur. In the carbonization stage, aromatic rings continue to condense and then convert into turbostratic graphite structure, and the diffraction peak at $2\theta \approx 25^\circ$ intensifies. The orientation of chain axis first decreases with the disappearing crystalline structure of PAN and reaches the minimum at the end of pre-oxidation. Subsequently, the orientation of chain axis increases with appearing of turbostratic structure during carbonization. The results obtained give a deep understanding of the microstructure development in the PAN fibers during pre-oxidation and carbonization, which is important for the preparation of high performance carbon fibers.

ACKNOWLEDGEMENTS We would like to thank Prof. Jie Liu and Prof. Liang-hua Xu at Beijing University of Chemical Technology for their help with pre-oxidation and carbonization of PAN fibers and the tensile strength measurements of single fibers. The samples were supplied by Weihai Tuozhan Fiber Co., Ltd and authors also thanks the Taishan Talents Project.

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